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THE EQUATION OF STATE OF POLYMER LIQUIDS AND GLASSES
AT ELEVATED PRESSURES

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ABSTRACT **UNPUBLISHED PRELIMINARY DATA**

By a combination of experimental isotherms and making use of theoretical results, we establish the validity of the theorem of corresponding states for chain liquids and derive an explicit expression for the reduced pressure - volume - temperature surface encompassing oligomer and high polymer liquids. For this purpose empirical Tait isotherms are employed with one adjustable parameter only, by showing that they describe experimental data for high polymer liquids also. One observes furthermore that the Tait relation remains valid below the glass transition temperature with only one of the parameters changing its functional dependence on temperature in the transition. We are able to conclude that a reduced equation of state describes polymer glasses also, with the same reducing parameters which characterize the liquid. This permits appropriate predictions at elevated pressure from volume - temperature studies of the glass at atmospheric pressure, combined with equation of state results of the liquid polymer. Our results thus support for both chain liquids and glasses the postulates formulated by others as a basis for a principle of corresponding states. A correction must be made, however, in computing enthalpies or cohesive energy densities for polymers with highly asymmetric units from equation of state properties by means of this principle. Deviations between the reduced experimental and theoretical equations of state at low temperatures are entirely determined by the characteristic failure of cell theory in respect to the internal pressure. At elevated temperatures, the theoretical thermal expansions are also in error. The principle of corresponding states and the general equation of state derived from it are, of course, unaffected

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ABSTRACT (cont.)

and serve as a guide for further theoretical developments. Finally, it turns out that the Tait equation describes the isotherms of partially crystalline branched polyethylene whereas it predicts larger compressibilities than are observed for linear crystalline polymethylene. Above the melting region we interpret the departures from the Tait relation for both polyethylene and polymethylene as due to crystallization effects and compute the variation of crystallinity with pressure.

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I. INTRODUCTION

The study of the properties of solids and liquids under high pressure is of considerable theoretical and practical interest. For high polymers, a certain amount of experimental work has followed in recent years Bridgman's pioneering efforts.

Recently we have been concerned with the results of cell theory in describing the thermodynamic properties of chain-type liquids, including high polymers.^{1,2,3} This theory conforms to a principle of corresponding states. At atmospheric pressure it accounts quantitatively for the thermal expansion and the cohesive energy density of oligomers and high polymers for reduced volumes \bar{V} not exceeding 1.2, but characteristically fails in respect to the internal pressure. However, the principle of corresponding states has been shown to remain valid in respect to all the quantities mentioned over the whole range of temperatures experimentally available at atmospheric pressure. This principle thus provides a guide for further developments in the theory of polymer liquids besides representing a practical tool for the computation of thermodynamic quantities in polymer systems not readily obtainable or available

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¹ R. Simha and A. J. Havlik, J. Am. Chem. Soc. 86, 197 (1964).

² V. S. Nanda and R. Simha, J. Phys. Chem., in press.

³ V. S. Nanda and R. Simha, J. Chem. Phys., in press.

otherwise.

Turning now to an analysis of chain liquids at elevated pressures, it would be inconvenient, if not impracticable to make direct comparisons between theory and, say, experimental isotherms or isochors. One would prefer to be able to base such comparisons on empirical equations fitted to the data. Several such equations have been given in the literature. For liquids the simplest of these appears to be the Tait equation, containing two adjustable parameters. For hydrocarbons in the lubricating range of molecular weights it has been shown to provide excellent fits to experimental isotherms up to several thousand bars, except at high temperatures.⁴ Moreover, it turns out that one of the parameters, C, a dimensionless quantity, assumes a universal value irrespective of structure and molecular weight of the hydrocarbon.⁴ The other, B, has ^{the} dimensions of pressure and is characteristic of the material and a function of temperature alone. We have previously commented on this behavior in terms of the cell theory³, but a detailed application was made to one compound only, as an example, namely $n - C_{15}H_{32}$, for which B had been explicitly evaluated in the published account⁴ of the high pressure work at the Pennsylvania State University.

In the present paper we examine the relation between theoretical and experimental isotherms for several types of chain liquids, including high polymers, over a wide range of temperatures and pressures up to about 2000 bars and establish the validity of the principle of corresponding states, even where theory fails. Previous tests of the principle have been carried out in a limited manner for n - paraffins.^{5,6}

⁴ Cutler, McMickle, Webb and Schiessler, J. Chem. Phys. 29, 727 (1958); W. G. Cutler, Thesis, Pennsylvania State University, 1955.

⁵ Prigogine, Bellemans and Naar-Colin, J. Chem. Phys. 26, 751 (1957); see also I. Prigogine, The Molecular Theory of Solutions, North Holland Publishing Co., Amsterdam, 1957.

⁶ J. Hijmans, Physica 27, 433 (1961).

This examination is carried out in terms of the Tait equation by showing first that it applies to amorphous high polymers as well and with the identical value of C obtained for hydrocarbons.⁴ The principle of corresponding states is thus reduced for our purposes to a universal functional relationship between the reduced volume at atmospheric pressure and the reduced quantity \tilde{B} . It turns out that the Tait equation also describes isotherms of polymers below their glass transition temperatures. Moreover, a principle of corresponding states obtains which enables one to predict the compressibility of the glassy polymer from characteristics of the liquid, viz. a combination of isobars at atmospheric pressure with isotherms or, with certain restrictions, cohesive energy densities. Finally, the Tait equation applies even to semicrystalline polymers. In addition to theoretical implications these results indicate applications and areas of fruitful experimental investigations.

II. GENERAL

Provided the principle of corresponding states is obeyed, the Tait equation assumes the following form in reduced variables, if C is a universal constant:³

$$1 - \tilde{V}_p / \tilde{V}_0 = C \ln (1 + \tilde{p} / \tilde{B}) \quad (1)$$

The reduced zero and finite pressure volumes \tilde{V}_p and \tilde{V}_0 are defined in terms of a characteristic volume V^* per chain or v^* per chain segment. The reduced pressure \tilde{p} equals $p/(E^*/V^*)$ and hence \tilde{B} equals $B/(E^*/v^*)$. Here E^* represents a characteristic energy per chain. Again, on subdividing the chain into segments and making use of the lattice model, one has $E^* = qz\epsilon^*$,⁵ with ϵ^* the maximum attractive energy between a pair of segments and $qz = s(z-2) + 2$, the number of intermolecular nearest neighbors of an s -mer. When two or more types of repeating units occur, the quantities E^* and V^* become suitable number averages. Similarly, when the molecular weight is not uniform, number average chainlengths must be used.

From eq. (1) we obtain the reduced compressibility

$$\tilde{\kappa} = C/(\tilde{B} + \tilde{p})[1 - C \ln(1 + \tilde{p}/\tilde{B})]^{-1} \quad (2)$$

which simplifies to C/\tilde{B} for $\tilde{p} \ll \tilde{B}$. The validity of the Tait equation implies that the coefficient B is a function of temperature solely. If it can be demonstrated that \tilde{B} is a universal function of a reduced temperature \tilde{T} or, equivalently, the reduced zero pressure volume, \tilde{V}_0 , then it follows that a reduced equation of state

$$\tilde{p} = \tilde{p}(\tilde{V}, \tilde{T}) \quad (3)$$

exists. The relation between \tilde{V}_0 and the reduced temperature $\tilde{T} = ckT/(qz\epsilon^*)$ has been discussed earlier.^{1,2} Here $3c$ represents the effective number of volume dependent degrees of freedom per chain.⁵ Combining this result with eq. (1) and the universal function $\tilde{B}(\tilde{V}_0)$, we shall obtain an explicit expression for the reduced volume-temperature-pressure surface, eq. (3), correct, of course, only within the range of applicability of the Tait relation.

The theoretical equation of state derived from cell theory⁵ and approximating the cell potential by a square well, has the form:²

$$\tilde{p}\tilde{V}/\tilde{T} = (1 - 2^{-1/6}\tilde{V}^{-1/3})^{-1} + (2\tilde{V}^{-2}/\tilde{T})(1.011\tilde{V}^{-2} - 1.2045) \quad (4)$$

From eq. (4) and the relations³

$$\tilde{V}_0 C = - (\partial \tilde{p} / \partial \tilde{V})_{\tilde{T}} / (\partial^2 \tilde{p} / \partial \tilde{V}^2)_{\tilde{T}}; \quad \tilde{B} = (\partial \tilde{p} / \partial \tilde{V})_{\tilde{T}}^2 / (\partial^2 \tilde{p} / \partial \tilde{V}^2)_{\tilde{T}} - \tilde{p} \quad (5)$$

we obtain the theoretical C and \tilde{B} as a function of \tilde{T} or \tilde{V}_0 , eq. (3) of ref. 3.

III. POLYMER AND OLIGOMER LIQUIDS

For the n - paraffins we make use of Cutler et al.'s data for C_{12} , C_{15} , C_{18} and their evaluation of B for a series of temperatures with $C = 0.0894$. The numerical values of the scale parameters V^* and $E^*/V^* = qz\epsilon^*/V^*$ are already known from studies of the volume - temperature curves and the cohesive energy densities respectively (see however below), combined with eq. (4).² We are thus able to define the lower portion of the $\tilde{B} - \tilde{V}_0$ function in Fig. 1, i.e. for $\tilde{V}_0 > 1.15$. We shall find this function for lower reduced temperatures by turning to high

polymers, provided they obey the Tait relation. For this purpose we make use of recent measurements by Hellwege et al.⁷ who investigated several liquid, glassy and semicrystalline polymers up to pressures of about 2 kilobars. As an example we show in Table I. the values of B computed from eq. (1) for polystyrene at 162.3°C and adopting $C = 0.0894$ as for the hydrocarbons.⁴ The maximum variation of B about the mean is less than 1.5%. Similar derivations are noted for polystyrene at temperatures between 100 and 250°C. When the temperature is low enough so that a glass transition occurs by the application of pressure, B, of course, increases systematically on approaching the transition interval. Table II. summarizes the mean B - values for liquid polystyrene.

The polystyrene used was a commercial sample. Moreover, the temperature range for the liquid polymer extends to 250°C. The presence of degradation and oxidation products under these conditions appears likely. Unfortunately, no characterizations at the start and completion of the experiments are available. Hence no parameters for polystyrene previously derived² will be used but the experimental $V_O - T$ data directly superimposed on the $\hat{V}_O - \hat{T}$ curve.² There is negligible scatter, the V^* differs insignificantly from the earlier values adopted and T/\hat{T} by less than 3%. However, the region $\hat{V}_O > 1.15$, defined by the n - paraffins in Fig. 1, can not be used to obtain the pressure reducing factor for polystyrene, since it corresponds to the highest temperature, viz. 250°C, and is therefore least reliable. Hence an alternative procedure was adopted for the evaluation of the $\hat{B} - \hat{V}_O$ relation. For moderate pressures we may write:

$$\alpha T = \kappa p_i \quad (6)$$

where α and p_i are the thermal expansivity and internal pressure respectively. We have shown previously² that p_i is not correctly represented by the theory, eq. (4), in contrast to α for $1 \leq \hat{V}_O \leq 1.20$ and that consequently κ is also in error.

⁷ K. H. Hellwege, W. Knappe and P. Lehmann, Kolloid.-Z. 183, 110 (1962).

Hence we may state

$$(\tilde{\kappa} \tilde{p}_i)_{\text{theor}} = (\tilde{\kappa} \tilde{p}_i)_{\text{exp}} \quad \text{or} \quad (C \tilde{p}_i / \tilde{B})_{\text{theor}} = (C \tilde{p}_i / \tilde{B})_{\text{exp}} \quad (6a)$$

On the left hand side of eq. (6a) we obtain all the quantities for a specified value of \tilde{V}_0 from eqs. (4) and (5) or Fig. 1 of ref. 3 and Fig. 3 of ref. 2.

On the right hand side C equals 0.0894 and \tilde{p}_i is found from Fig. 3, ref. 2 for $1.09 \leq \tilde{V}_0 \leq 1.24$. One can therefore obtain \tilde{B}_{exp} from eq. (6a) in the region $1.09 \leq \tilde{V}_0 \leq 1.12$, the upper limit being determined by the inaccuracy of the Tait relation at high temperatures in respect to the limiting compressibility and the lower one by the availability of \tilde{p}_i 's.² From these results and the B - value, appropriate to this region the reducing factor B/\tilde{B} is derived and the remaining portion of the experimental curve, Fig. 1, defined. The point for $\tilde{V}_0 = 1.152$, corresponding to the highest temperature, viz. 248.9°C shows an appreciable departure from the curve. The smaller value of \tilde{B} is in qualitative accord with the appearance of degradation products at such a high temperature.

Hellwege et al.⁷ give high pressure data for a polymethyl methacrylate (Resartglas) and a polyvinyl chloride (Vestolit SSpL) sample over a sufficiently wide range of temperatures to provide a further test of the principle of corresponding states. From the results at atmospheric pressure, we derive the reducing parameters V^* and T/\tilde{T} shown in Table III. These polymers also follow the Tait equation, see Tables I. and II. There appears to be a slight systematic trend in polyvinyl chloride. However, the data are too limited for any definite conclusions. The ratios p/\tilde{p} obtained at one temperature suffice to place the B 's for the two polymers on Fig. 1 and to provide a further confirmation of the principle of corresponding states. It should be recalled in this connection that the $\tilde{p}_i - \tilde{V}$ function used in constructing the experimental curve in Fig. 1 for $\tilde{V}_0 < 1.15$ is based on n - paraffin data.² This provides an additional confirmation of the principle of corresponding states as well as the accuracy of the indirect procedure used to arrive at the \tilde{B} - values.

Table III. summarizes the numerical values of the characteristic volume, pressure and temperature parameters for the three polymer systems. The order of the V^* is as expected and the T/\bar{T} appear reasonable. For polystyrene the volume and temperature shift factors are close to those obtained earlier.² However, a considerable discrepancy in respect to the quantity ϵ^*s/n is noted. Earlier² we found 397×10^{-16} from published swelling data and 436×10^{-16} from enthalpies of vaporization for monostyrene and application of the corresponding states principle to cohesive energy densities. In comparing monostyrene with a styrene unit in the polymer, differences can be expected. The discrepancies encountered here, however, are too large. At this point we recall one of the requirements of the corresponding states principle namely, that the potential energy function between a pair of segments assume the identical analytical form for all substances considered. Actually, the theoretical eq. (4) is based on the spherically symmetrical 6 - 12 potential. This should be a fair assumption for a symmetrical polymer such as polymethylene. However, if the same potential is applied to the highly asymmetrical styrene unit, it requires at least readjustments in the energy scale factor ϵ^* on going from one set of properties to another, as we actually find.

For symmetry reasons, this problem can not be important for the n - paraffins, used to determine the \bar{B} - function for $\bar{V}_0 > 1.15$ and through \bar{p}_1 also the other region. Moreover we have shown earlier³ that good agreement between experimental and theoretical \bar{B} results by using the scale factor E^*/V^* derived from cohesive energy densities in the neighborhood of $\bar{V}_0 = 1.15$, the region in which the experimental and theoretical \bar{p}_1 are close.² This is again seen in Fig. 1, which exhibits the theoretical \bar{B} - function derived from eqs. (4) and (5).

We can formally retain the pressure reducing factors derived from the enthalpies of vaporization for the equation of state by replacing in eq. (1) \bar{B} by $\gamma \bar{B}$ where γ is the ratio of the reducing factor (E^*/V^*) determined from the

c.e.d. and the equation of state respectively. Thus for polystyrene γ would vary between 1.37 and 1.25 depending on whether enthalpies of vaporization for monostyrene or swelling data for the polymer are used. This factor is also included in the tabulation of the ratio $3c/n$, Table III. The numerical value for polymethyl methacrylate is large and close to that of polystyrene and presumably for similar reasons, i.e., the presence of degrees of freedom associated with the side groups. Polyvinyl chloride occupies an intermediate position between polymethylene and polystyrene or polydimethyl siloxane.² We would expect γ here to be smaller than for polystyrene, and might speculate that the differences arise from^a reduction in the internal torsional frequencies, as compared with polymethylene.

In Fig. 1 is shown also the theoretical \tilde{B} - function, derived from eqs. (4) and (5). It will be noted that there is a region of minimum deviation between experimental and theoretical B , the latter becoming increasingly smaller than the former. This trend is consistent with and reflects the relation between experimental and theoretical p_i 's noted earlier.² That is, for $\tilde{V} < 1.2$, the thermal expansivities α are correctly given by the theory, and the deviations in p_i entirely determine those in respect to κ and hence B . At sufficiently elevated temperatures, on the other hand, both the theoretical α and the p_i are too large, the former predominating.

We can now formulate explicitly the complete reduced equation of state for oligomers and high polymer liquids obeying the Tait relation. \tilde{V}_0 in eq. (1) is given as a function of \tilde{T} for $\tilde{V}_0 < 1.2$ by eq. (4), setting the left hand side equal to zero. For $\tilde{V}_0 \geq 1.2$, the following empirical equation obtains[†]:

$$\begin{aligned} \log (\tilde{V}/1.017) = & 16.058 + 58.494 \cdot \log (\tilde{T}/1.272) + 81.615 \cdot \log (\tilde{T}/1.272)^2 \\ & + 51.210 \cdot \log (\tilde{T}/1.272)^3 + 12.121 \cdot \log (\tilde{T}/1.272)^4 \end{aligned} \quad (4a)$$

[†] This result follows from a combination of eq. (3), ref. 1 and eq. (8), ref. 2.

Finally we derive from Fig. 1 the result:

$$\tilde{B} = \tilde{B}_{\text{theor}} + 0.00559 - 0.0806 (\tilde{V}_0 - 1.15) + 6.457 (\tilde{V}_0 - 1.15)^2 - 44.04 (\tilde{V}_0 - 1.15)^3 \quad (4b)$$

where \tilde{B}_{theor} is given by eq. (3), ref. 3.

The preceding results enable us now to predict the pressure - volume relation and compressibility for any other polymer or oligomer liquid, provided a) the Tait equation is applicable, b) the volume - temperature relation at atmospheric pressure has been obtained and c) the reducing factor for B is known. The latter may alternatively be obtained from a high pressure determination, a direct measurement of the internal pressure at a single volume and the $\tilde{p}_i - \tilde{V}$ curve² or from the enthalpy of vaporization of an oligomer and the relation between reduced cohesive energy density and \tilde{V} .² In the light of the observations with polystyrene, however, a direct density measurement at one pressure at least, will be the reliable method for asymmetric structures.

IV. POLYMERS BELOW THE GLASS TRANSITION TEMPERATURE

We shall discuss isotherms for temperatures below the transition interval, and look first for analytical representations. It turns out that the Tait equation describes very nicely the high pressure ^{properties} of the amorphous polystyrene, polymethyl methacrylate and polyvinyl chloride systems⁷ with the previous value of C. The behavior of B as a function of pressure is illustrated in Table IV. and the mean B's are summarized in Table V. The maximum deviations from these averages generally do not exceed 1%.

We have no theory of the equation of state of a glass, corresponding to eq. (4). We ask whether a corresponding states theorem applies to the glass similar to the liquid. If the answer will be in the affirmative, the reducing parameters for pressure and volume are fixed by properties in the liquid range, since they involve only the characteristics of the pair

potential, unless the coordination number z of the quasi - lattice is permitted to undergo a change in the transition. Thus no adjustable scale factors for the glass are at our disposal. Fig. 2 shows \tilde{B} as a function of \tilde{V}_0 , using Tables III. and V., and confirms the validity of the principle of corresponding states for polymeric glasses in respect to the isotherms, at least.

Again it is convenient to represent this result in analytical form. We find:

$$\begin{aligned}\tilde{B}_g &= 0.6274 - 7.40 (\tilde{V}_0 - 1.055) + 39.2 (\tilde{V}_0 - 1.055)^2; \quad 1.07 \leq \tilde{V}_0 \leq 1.04 \\ \tilde{B}_g &= 7.1585 - 6.2000 \tilde{V}; \quad 1.07 < \tilde{V}_0 < 1.09\end{aligned}\quad (4c)$$

Not only is \tilde{B} considerably larger for the glass than in the liquid state, but the variation with \tilde{V}_0 is larger.

In order to obtain a complete picture for the glassy state, the isobars at atmospheric pressure must be considered. We shall not undertake a detailed study of volume - temperature data here but restrict ourselves to the limited results on the three glasses⁷ described in Fig. 2, ^{and} extending over a temperature range from about 20 to 110°C. We retain not only the V^* - values, but also the reduced temperatures given in Table III., thus postulating tentatively, that the number of volume dependent degrees of freedom does not change on passing through the transition. No disposable parameter remains therefore for the glass. It is possible, within a scatter of not more than $\pm 0.5\%$, to ^{construct} a universal curve. It is not shown explicitly, because an adequate representation requires a more thorough investigation of experimental results on glasses. Within the limitations stated the principle of corresponding states is validated for glasses, with the same characteristic pressure, volume and temperature variables as the liquid, but a different $\tilde{p} - \tilde{V} - \tilde{T}$ surface, of course.

This result is of great practical importance, since it permits a prediction of high pressure properties from the isobars at atmospheric pressure and a

knowledge of the scale factors from studies of the liquid polymer. Finally eqs. (4), (4a), (4b) and (4c) conveniently yield the changes $\Delta\kappa$ in compressibility at the glass transition temperature at any pressure.

V. CRYSTALLIZABLE POLYMERS

Hellwege et al.⁷ have also determined the isotherms of a linear (Marlex 9) and a branched (Lupolen 1811H) polyethylene and observed the change of melting range with pressure. Extensive measurements up to 10 kilobar on a branched sample (not otherwise specified) in the region of partial crystallinity have been undertaken by Weir.⁸ We believe that his results for $t \geq 60^\circ\text{C}$ are in error, as the volume changes reported between 1000 and 2000 atmospheres are actually larger than those between 1 and 1000.[†] No such difficulty appears in Hellwege et al.'s data⁷ under similar conditions.

If the Tait equation is applied to these polymers above the melting range, one finds a systematic decrease of B with increasing pressure for both the linear and the branched polymer. This is illustrated in Fig. 3. Such a behavior would be consistent with an actual crystallization effect at high pressures, where B decreases most rapidly, and hence an additional decrease in volume. The initial decrease in B may be indicative of some kind of ordering effect. In the absence of concrete experimental evidence we are inclined to take this view because the behavior of n - paraffins follows Tait's equation so well.⁴

If we provisionally accept this interpretation, the degree of "order" as a function of pressure may be estimated from a comparison of the Tait parameter B_0 which would obtain for the "normal" material and the actual B_p observed. The former can be derived from the $\bar{V} - \bar{V}_0$ function for amorphous polymers, since the

⁸ C. E. Weir, J. Res. Natl. Bur. Stands. 53, 245 (1954)

[†] A similar result obtains for a 1:1 copolymer of ethylene and tetrafluoroethylene at all temperatures.

volume and pressure scale factors for polymethylene are available from the n - paraffins. In this manner the series of points in Fig. 3 are obtained. It appears that within the scatter shown the difference $B_0 - B$ is a function of pressure only and characteristic of the sample. Also, $B_0 - B$ is larger for the more highly crystallizable linear polymethylene. At the highest temperature, i.e. 203°C , degradation may have^{caused} the B_0 - value used in Fig. 3 to be too large.

Let X denote the fractional degree of "order", and V_{pa} and V_{pc} the respective volumes of the amorphous and ordered regions at a pressure p and a fixed temperature. Then

$$V_p = X V_{pc} + (1 - X) V_{pa}$$

If V_{pa} and V_p are assumed to be determined by the Tait equation with $B = B_0$ and B_p respectively, and an estimate of V_{pc} is available, the function $X(p)$ can be computed. The results are exhibited in Fig. 4 for the linear polymer at 150.4°C and for the branched sample at 140.5°C . The following numerical assumptions are made: $v_{oc} = 1.000$ cc/g at $t = 20^\circ\text{C}$, the average value of α_c was determined to 3.4×10^{-4} , by linear interpolation between 19.4 and 59.6°C for the highly crystalline sample and used throughout and it is assumed that at all temperatures and pressures $(V_{oc} - V_{pc}) / V_{oc} = 1/3 (V_{oa} - V_{pa}) / V_{oa}$. These assumptions influence the numerical values of X , particularly as X becomes large, but do not alter the general trend of the curves. In Fig. 4 we note a sharp rise, more pronounced for the linear polymethylene, ^{when} solidification begins under pressure as is indicated by the vertical lines drawn according to ref. 7. These results support our interpretation. It is instructive to compare the $X - p$ function with the analogous $X - T$ function at atmospheric pressure exhibited in Fig. 5, which shows analogous characteristic differences between crystalline polymethylene and polyethylene. We want to stress that the amorphous volumes v_a as a function of temperature and pressure are

determined here by means of the corresponding states principle rather than by extrapolations from above the melting point. We give further supporting evidence for this interpretation below. Direct observation of these polymers under pressure and study of the pressure behavior of the crystal would be required for more quantitative conclusions.

Turning now to temperatures well below the melting range of the branched sample, a Tait representation is suggested, arguing that the presence of a large fraction of amorphous material should permit this. The results are illustrated in Table VI. which indicates fluctuation in the B - values of about 2%. In contrast, the linear polymethylene is characterized by a systematic increase of B with increasing p . Table VII. shows the average values for polyethylene. Weir's data⁸ also conform to the Tait equation for $t < 60^{\circ}\text{C}$. Both results may be understood in the light of the earlier discussion. In the branched polymer, the main contribution to the compression arises from the amorphous regions, and no further crystallization is produced by the application of pressure. In the crystalline sample, the Tait equation would not be expected to hold to begin with, and we observe that the crystal is less compressible than would be predicted by this relation.

VI. CONCLUSIONS

We have established the existence of a universal equation of state over a wide range of temperatures and pressures, which applies to liquids of short chains as well as high polymers. For chains with symmetric non-polar units which can be reasonably characterized by a spherically symmetrical interaction potential the numerical values of the reducing parameters can be uniquely defined to represent both equation of state properties and enthalpies of vaporization or cohesive energy densities. For asymmetric structures, on the other hand, the assumption of an effective spherical symmetry requires the introduc-

tion of an asymmetry term in discussing consistently both sets of properties. The polar systems investigated here and earlier^{1,2} obey the same reduced equation of state as non-polar molecules and it will be interesting to compare enthalpies of vaporization. Our results, obtained for chain liquids of very diverse structures, lend support with the restriction noted, to the general assumptions underlying the principle of corresponding states, namely:^{5,6}

a) the subdivision of the chain into a definite number of segments and the additivity of the segment interactions with a fixed number of nearest neighbors and b) the separation of the degrees of freedom into internal and external ones independently of the temperature. It is possible to extend the principle of corresponding states to glasses, at least beyond the transition interval, without making any change in the reducing parameters.

The present results are in accord with and extend our earlier conclusions² regarding the position of the statistical mechanical theory in what amounts to essentially the LJD approximation. In particular they relate the limitations in predicting high pressure properties from theory to the failure of the approximation in respect to the configurational entropy, at least for $\bar{V} < 1.20$, where the thermal expansion is correctly given. Finally we note that any detailed theory which would take explicitly into account the effect of intra and inter-molecular interactions on the degrees of freedom^{for polymers} with internal rotation barriers, must lead to a principle of corresponding states.

TABLE I
 VARIATION OF TAIT PARAMETER B (KILOBAR) WITH PRESSURE
 FOR HIGH POLYMER LIQUIDS

p/0.9806	Polystyrene t = 162.3°C	Polymethyl- methacrylate t = 129.7°C	Polyvinyl chloride t = 97°C
200	1.15	1.56	1.89
400	1.13	1.55	1.92
600	1.125	1.55	1.94
800	1.14	1.54	1.97
1000	1.14	--	1.98
1200	1.14	--	--
1400	1.15	--	--
1600	1.15	--	--
1800	1.14	--	--
2000	1.13	--	--

TABLE II
 AVERAGE VALUES OF TAIT PARAMETER B (BAR) FOR HIGH POLYMER
 LIQUIDS AT A SERIES OF TEMPERATURES

Temp., °C	248.9	229.0	202.8	178.7	162.3	145.2	136.7	126	115.4
Polystyrene	730	837	952	1056	1138	1239	1305	1363	1450
Temp., °C	139.3	129.7	119.8	109.3					
Polymethyl methacrylate	1430	1545	1652	2145					
Temp., °C	97.0	90.6	82.0						
Polyvinyl chloride	1982	2088	2200						

TABLE III

CHARACTERISTIC PARAMETERS FOR HIGH POLYMERS DERIVED
FROM HIGH PRESSURE MEASUREMENTS

	T/\bar{T}	N_{AV}^*/n cc/mole	$(\gamma\epsilon^*s/n) \times 10^{16}$ erg/molecule	$r \ 3c/n$
Polystyrene	5200	47.9	318	1.33
Polymethyl- methacrylate	4780	39.7	360	1.53
Polyvinyl chloride	4555	21.1	232	1.11

TABLE IV

VARIATION OF TAIT PARAMETER B (KILOBAR) WITH PRESSURE
FOR HIGH POLYMER GLASSES AT 20°C

p/0.9806	Polystyrene	Polymethyl- methacrylate	Polyvinyl chloride
400	3.14	3.44	3.56 ₅
600	3.13	3.46	3.61
800	3.11	3.46	3.61 ₅
1000	3.12	3.45	3.58
1200	3.13	3.42	3.59
1400	3.13	3.41	3.58
1600	3.12	3.41	3.56 ₅
1800	3.11	3.41	3.55
2000	3.07	3.40	3.53

TABLE V

AVERAGE VALUES OF TAIT PARAMETER B (BAR) FOR HIGH POLYMER
GLASSES AT A SERIES OF TEMPERATURES

Temp., °C	20.0	51.0	60.0	60.5	100.0	109.3
Polystyrene	3118	--	--	2715	--	--
Polymethyl- methacrylate	3429	--	2886	--	2443	2249
Polyvinyl chloride	3576	3304	--	--	--	--

TABLE VI

VARIATION OF TAIT PARAMETER B (KILOBAR) WITH PRESSURE FOR
BRANCHED (20°C) AND LINEAR (19.4°C) POLYETHYLENE

p/0.9806	Branched t = 20°C	Linear t = 19.4°C
600	2.38	3.92
800	2.38	3.94
1000	2.40	3.95
1200	2.43	3.99
1400	2.45	4.05
1600	2.45	4.10
1800	2.44	4.12
2000	2.43	4.15 ₅

TABLE VII

AVERAGE VALUES OF TAIT PARAMETER B (BAR) FOR BRANCHED
POLYETHYLENE AT A SERIES OF TEMPERATURES
BELOW THE MELTING RANGE

20°C	40.8°C	60.1°C	79.8°C
2420	1991	1634	1295

LEGENDS FOR FIGURES

Fig. 1. Reduced Tait parameter \bar{B} as a function of the reduced volume \bar{V}_0 at atmospheric pressure. Lower curve, theoretical³, eqs. (4) and (5) in text. Upper curve, eq. (4b). Experimental:^{4,7} n - paraffins: Δ n - C₁₈, Δ n - C₁₅, Δ n - C₁₂, Δ , eq. (6a); polystyrene \square ; polymethyl methacrylate \bigcirc ; polyvinyl chloride \square .

Fig. 2. Reduced Tait parameter \bar{B} for high polymer glasses as a function of the reduced volume \bar{V}_0 at atmospheric pressure. Curve, eq. (4c). Experimental:⁷ polystyrene \square ; polymethyl methacrylate \bigcirc ; polyvinyl chloride \square .

Fig. 3. Difference between atmospheric pressure, B_0 , and actual Tait parameter as a function of pressure (0.9806 x bar) for several temperatures, °C, above the normal melting range. Polyethylene: \bigcirc 174.5, \bigcirc 150.7, \bigcirc 140.5. Polymethylene: \square 203.0; \square 185, \square 172, \square 161.2, \square 150.4.

Fig. 4. Percentage crystallinity as a function of pressure (0.9806 x bar), computed from Tait parameters at temperatures above the normal melting range. Lower curve, polyethylene at 140.5°C. Upper curve, polymethylene at 150.4°C. Vertical lines indicate pressure at end of melting range according to Hellwege et al.⁷

Fig. 5. Percentage crystallinity as a function of temperature at atmospheric pressure, computed from specific volumes by means of corresponding states principle for amorphous phase. Lower curve, polyethylene; upper curve, polymethylene.

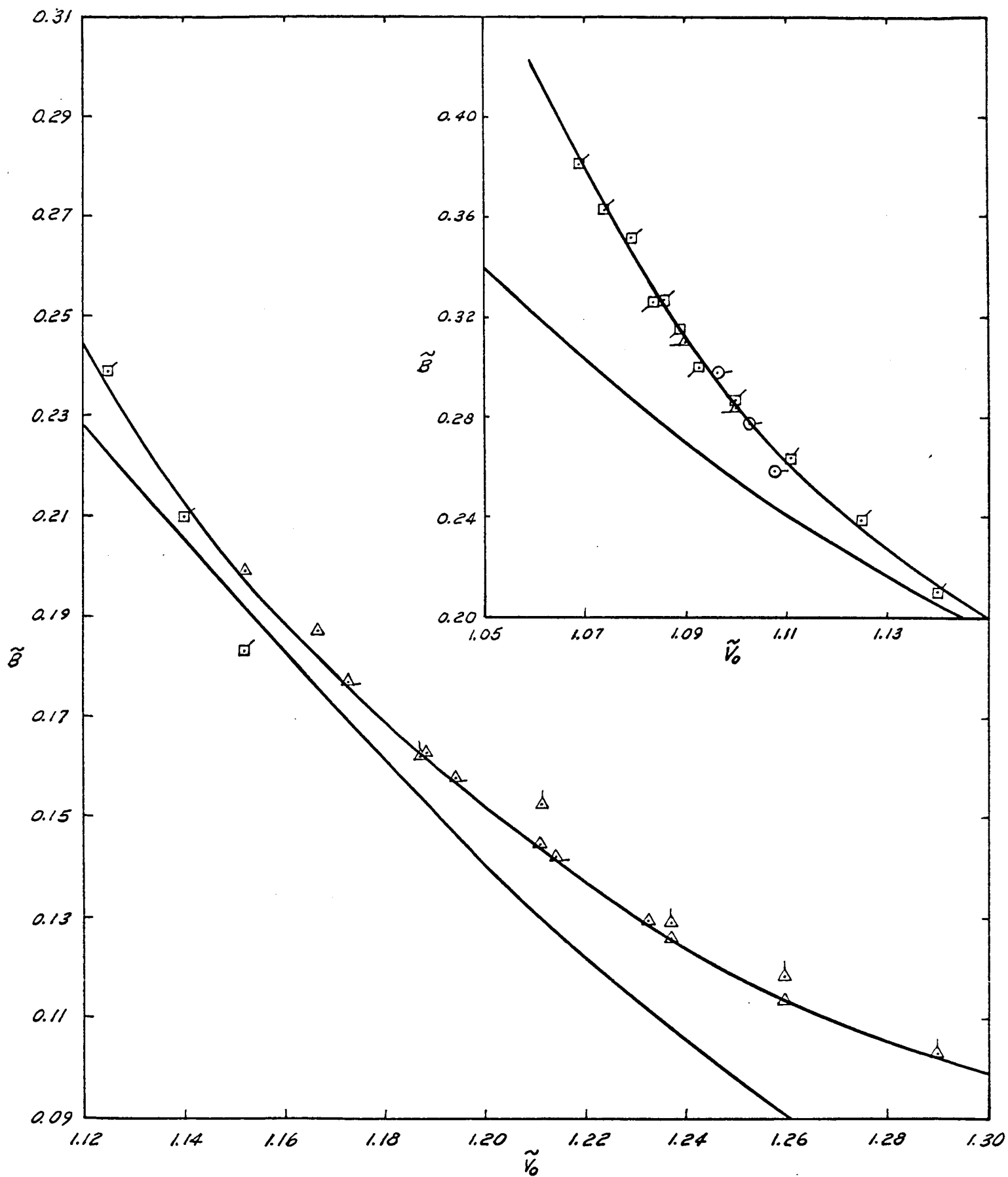
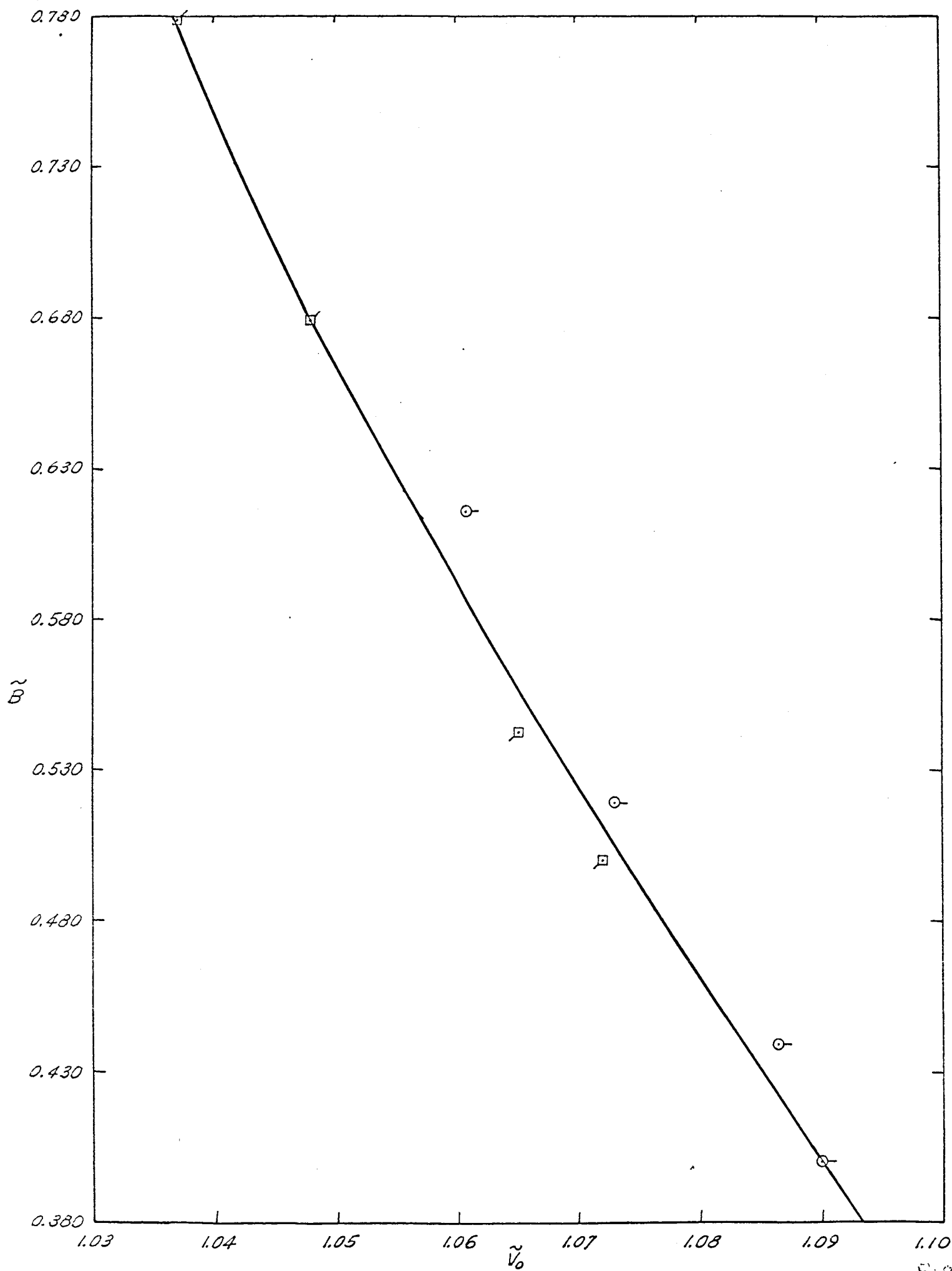
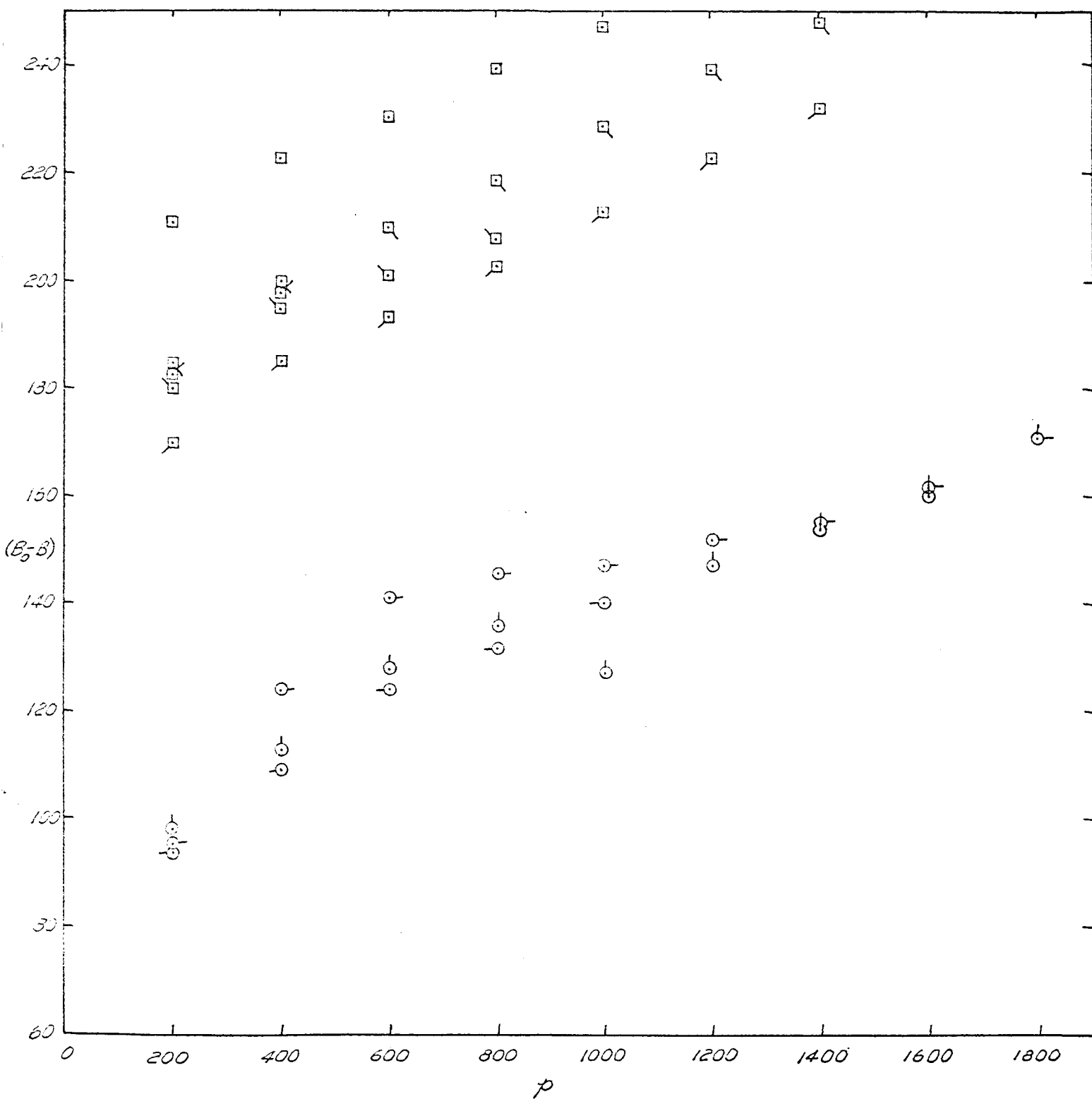
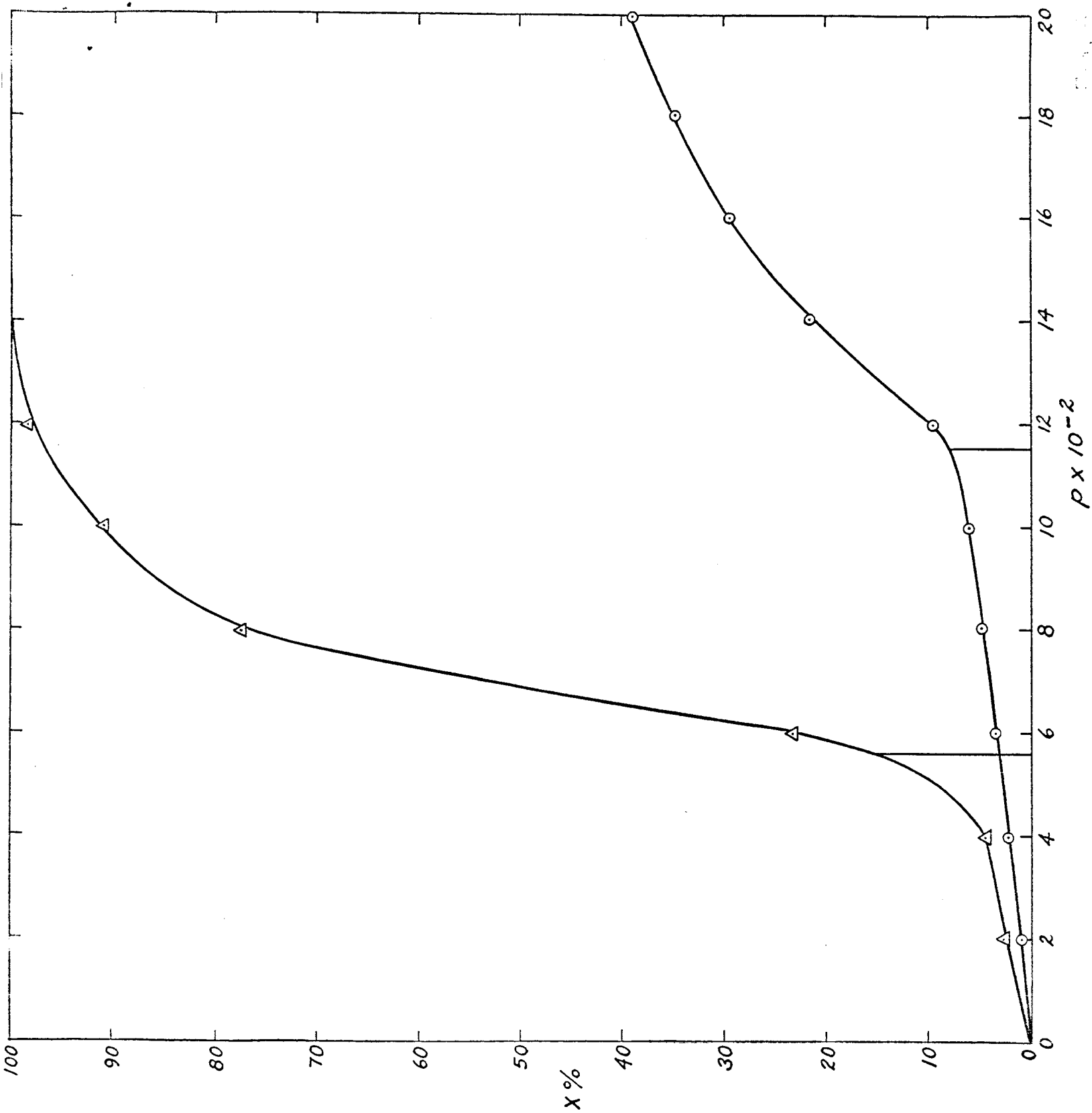


Fig. 1.







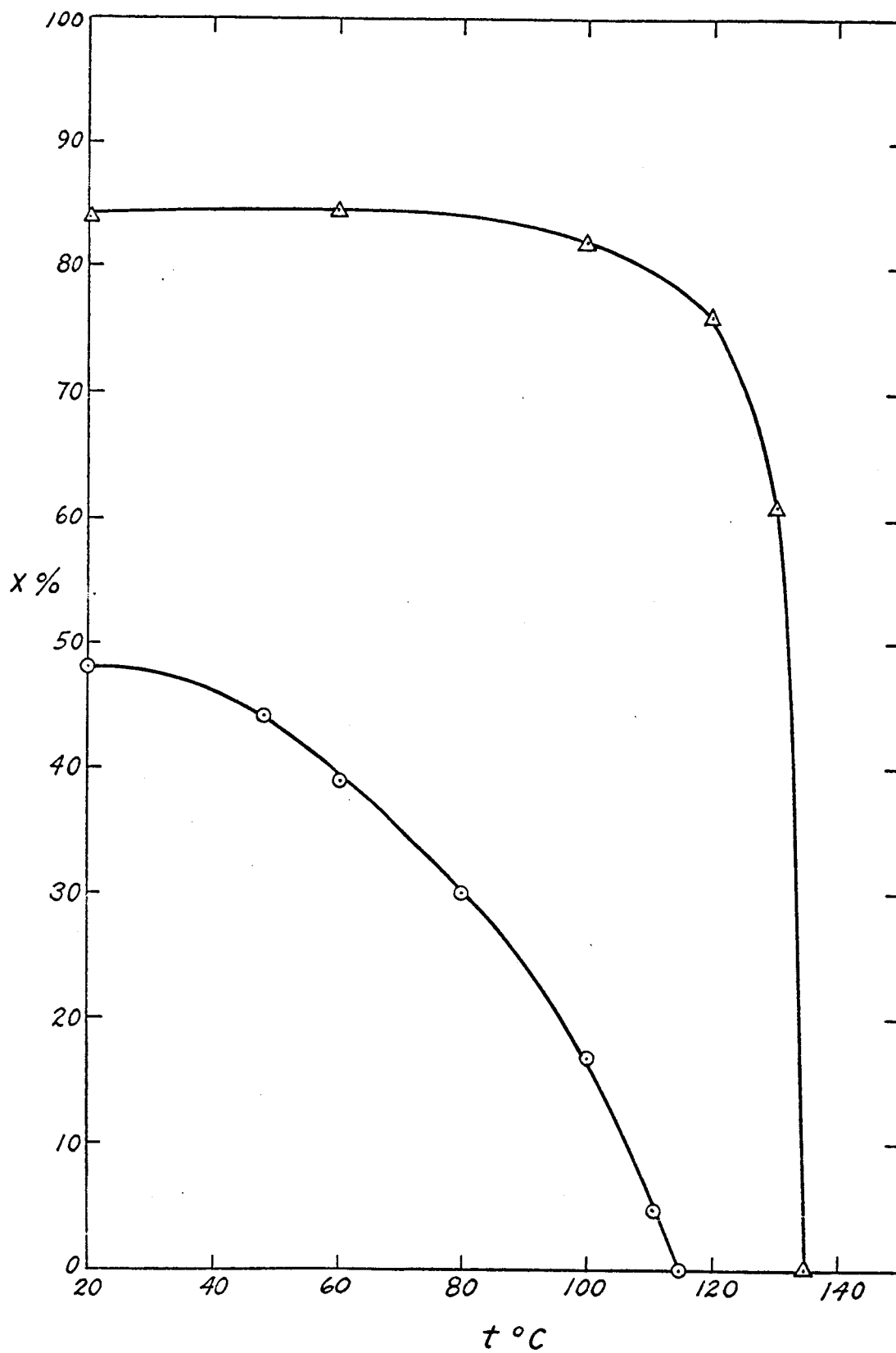


Fig. 5